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#3

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Principal Investigator: Bredas, Jean-Luc E.
Award ID: 0342321
Organization: GA Tech Res Corp - GIT
Title:
Electronic, Optical, and Interfacial Properties of pi-Conjugated Materials

Project Participants

Senior Personnel

Name: Bredas, Jean-Luc
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Coropceanu, Veaceslav
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Zojer, Egbert
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Beljonne, David
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Cornil, Jerome
Worked for more than 160 Hours: Yes
Contribution to Project:

Post-doc

Graduate Student

Name: Risko, Chad
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Lancaster, Kelly
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Sanchez-Carrera, Roel
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Leclercq, Amalia
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Fink, Christian

Worked for more than 160 Hours: Yes
Contribution to Project:

Undergraduate Student

Name: Zhong, Jim
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Stables, Jeffrey
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Wahl, Mark
Worked for more than 160 Hours: Yes
Contribution to Project:

Name: Malykhin, Alexey
Worked for more than 160 Hours: Yes
Contribution to Project:

Technician, Programmer

Other Participant

Research Experience for Undergraduates

Organizational Partners

Georgia Institute of Technology
Set-up funding for Jean-Luc Bredas.

Belgian National Fund for Scientific Res
Provided funding for extended stays at Georgia Institute of Technology for David Beljonne and Jerome Cornil.

Other Collaborators or Contacts

Collaborators with S. R. Marder (Georgia Institute of Technology), B. Kippelen (Georgia Institute of Technology), R. H. Friend (Cavendish Laboratory, Cambridge University, UK), N. Gruhn (University of Arizona), D. Frisbie (University of Minnesota), W. R. Salaneck (University of Linkoping, Sweden), A. Kahn (Princeton).

Activities and Findings

Research and Education Activities:

Our research revolved around four major axes: (i) intra- and inter-molecular self-exchange electron-transfer reactions; (ii) energy-transfer processes including resonant energy transfer (iii) photo-induced electron-transfer processes; and (iv) characterization of organic/organic heterojunctions and of simple metal/conjugated molecule interactions. Point (i) relates to the transport mechanism and is a key process in all applications of semiconducting polymers and oligomers. Point (ii) has to do in particular with color tuning and loss mechanisms in organic

light-emitting diodes and with exciton migration in organic solar cells. Point (iii) is at the heart of the charge separation process, critical in the operation of photodetectors and solar cells as well as photorefractive devices. Point (iv) expanded on our earlier work on metal/organic interfaces by addressing the electronic nature of organic/organic interfaces that are found in a variety of devices.

Findings: (See PDF version submitted by PI at the end of the report)

See attached Findings PDF file.

Training and Development:

The continuous feedback loop between theory and experiment, as well as the numerous collaborations with experimentalists, that form the basis of our research program provide our students and research associates with a strongly multi-disciplinary environment. In addition, regular group meetings are conducted with the groups of Professor S.R. Marder (a synthetic materials chemist), Professor J.W. Perry (a spectroscopist), and Professor B. Kippelen (a device electrical engineer), who are all interested in the electronic and optical properties of pi-conjugated materials.

Our research program on conjugated materials is also a major source of input for the graduate course on 'Chemistry of Electronic and Optical Materials' that has been newly developed at the Georgia Institute of Technology; this course has been expanded as a two-semester course in 2004-2005. It fed as well into the 'Fundamentals of Chemistry' course that I taught in Fall 2005.

Outreach Activities:

The Bredas group actively participates in Georgia's GIFT ('Georgia Intern Fellowships for Teachers') and STEP ('Student and Teacher Enhancement Partnership') programs.
In the 2004 summer, the GIFT program has given a teacher from a metro-Atlanta high school, Mrs. Anne Granville from Norcross High School, the opportunity to have a two-month summer research experience in the group, to develop computational skills, and to work on the improvement of an AP Chemistry course, with interactions remaining active throughout the school year: for instance, a member of Bredas' group, Dr. Demetrio Filho, has visited Norcross High School several times and a high-school student of Mrs. Granville, Justin Edward, worked half-time in our group during the 2005 summer.

The STEP program seeks to improve the teaching-related communication and leadership skills of Georgia Tech graduate students and to use the exceptional scholarly expertise available at Georgia Tech to assist in increasing the mathematics and science performance of Atlanta-area school students. One of the female graduate students in our Bredas group, Kelly Lancaster, was a STEP Fellow in 2004-2005, linked with Tri-cities High School, a minority high school located in East Point. Kelly Lancaster's high-school students visited Georgia Tech several times, toured our facilities, and attended a presentation given by a senior graduate student in our group, Amalia Leclercq.

In addition, the Bredas group participates in the SURE (Summer Undergraduate Research in Engineering/Science) Program at Georgia Tech. SURE is a ten-week summer research program designed to attract qualified minority students into graduate school in the fields of engineering and science. Approximately thirty students of at least junior-level undergraduate standing are recruited on a nationwide basis and paired with both a faculty and a graduate student mentor to undertake research projects in the College of Engineering, College of Sciences, and the Packaging Research Center. The students are housed on campus, and in addition to a $600 travel allowance, are provided with a meal plan and a $5,000 stipend. Aside from their own research projects, the participants are provided with a series of seminars and field trips to expose them to the various topics of interest, both at Georgia Tech and in the Atlanta area. At the conclusion of the program, the students prepare both oral and written summaries of their research projects. The program has received highly favorable evaluations from the past participants. It is hoped that this unique experience will encourage these students to become applicants for graduate school in ensuing years. In the 2005 summer, the Bredas group hosted Ms. Jelaunica Tigner, a female African-American, who is currently completing her senior year at Tuskegeee University in Alabama and is applying to graduate schools.

The Bredas group has been actively involved in the 'Atlanta Undergraduate Research Association (AURA)', which includes a diverse set of schools (including HBCs) in the Atlanta area (Agnes Scott College, Clark-Atlanta University, Emory University, Georgia Perimeter College, Georgia Tech, Georgia State University, Morehouse College, and Spelman College) and aims at promoting undergraduate research. The diversity in this set of schools exists at many levels such as institutional classification, total student enrollment, and the gender and ethnic profiles of their students. All of these issues can play a role in the intellectual development of our students, and sensitivity to these issues is an integral component of all our educational activities. In 2004-2005, an undergraduate student from Emory, Jim Zhong, was funded by AURA to do research in our group on an NSF-related topic; he was followed the following year by an undergraduate from Georgia Perimeter College, Jeffrey Stables.

We have initiated a strong connection with Norfolk State University, a minority institution in Virginia. Dr. Bredas visited the Center for

Materials Research at NSU on Sept. 02-03, 2004 and presented a seminar on: 'Charge Transport and Charge Recombination Processes in Organic Semiconductors', that was attended by many students. A collaboration has been started with Dr. Suely Black at NSU, which resulted in one of Dr. Black's master's students spending a few weeks at Georgia Tech over the 2006 summer.

See also the 'Contribution to Human Resource Development' section.

Journal Publications

V. de Halleux, J.P. Calbert, P. Brocorens, J. Cornil, J.P. Declercq, J.L. Bredas, and Y. Geerts, "1,3,6,8-Tetraphenylpyrene Derivatives: Towards Fluorescent Liquid Crystalline Columns?", Advanced Functional Materials, p. 649, vol. 14, (2004). Published

P. Marsal, I. Avilov, D.A. da Silva Filho, J.L. Bredas, and D. Beljonne, "Molecular Hosts for Triplet Emission in Light Emitting Diodes: A Quantum-Chemical Study", Chemical Physics Letters, p. 521, vol. 392, (2004). Published

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C. Risko, G. P. Kushto, Z. H. Kafafi, and J.L. Bredas, "Electronic properties of silole-based organic semiconductors", Journal of Chemical Physics, p. 9031, vol. 121, (2004). Published

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D. Beljonne, G. Pourtois, M.A. Ratner, and J.L. Bredas, "Pathways for Photoinduced Charge Separation in DNA Hairpins", Journal of the American Chemical Society, p. 14510, vol. 125, (2003). Published

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D.A. da Silva Filho, R. Friedlein, V. Coropceanu, G. Ohrwalf, W. Osikowicz, C. Suess, S.L. Sorensen, S. Svensson, W.R. Salaneck, and J.L. Bredas, "Vibronic Coupling in the Ground and Excited States of the Naphtalene Cation", Chemical Communications, p. 1702, vol. 15, (2004). Published

O. Kwon, V. Coropceanu, N.E. Gruhn, J.C. Durivage, J.G. Laquindanum, H.E. Katz, J. Cornil, and J.L. Bredas, "Characterization of the Molecular Parameters Determining Charge Transport in Anthradithiophene", Journal of Chemical Physics, p. 8186, vol. 120, (2004). Published

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C. Lambert, C. Risko, V. Coropceanu, J. Schelter, S. Amthor, N. Gruhn, J. Durivage, and J.L. Bredas, "Electronic Coupling in Tetraanisylarylenediamine Mixed-Valence Systems: The Interplay between Bridge Energy and Geometric Factors", Journal of the American Chemical Society, p. 8508, vol. 127, (2005). Published

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E. Engel, K. Schmidt, D. Beljonne, J.L. Bredas, J. Assa, H Frob, K. Leo, and M. Hoffmann, "Transient Absorption Spectroscopy and Quantum-Chemical Studies of Matrix-Isolated Perylene-Derivative", Physical Review B, p. 245216/1, vol. 73, (2006). Published

E.G. Kim, K. Schmidt, W.R. Caseri, T. Kreouzis, N. Stingelin-Stutzmann, and J.L. Bredas, "Magnus? Green Salt Revisited: Impact of Platinum-Platinum Interactions on Electronic Structure and Carrier Mobilities", Advanced Materials, p. 2039, vol. 18, (2006). Published

K. Schmidt, V. Coropceanu, J.L. Bredas, S. Brovelli, F. Meinardi, R. Tubino, C. Bazzini, and T. Caronna, "Excited-State Properties and Emission Spectra of Nonplanar Heterocyclic Helicenes", Journal of Physical Chemistry, p. 11018, vol. 110, (2006). Published

V. Coropceanu, T. Nakano, N.E. Gruhn, O. Kwon, T. Yade, K. Katsukawa, and J.L. Bredas, "Probing Charge Transport in p-Stacked Fluorene-Based Systems", Journal of Physical Chemistry B, p. 9482, vol. 110, (2006). Published

R.S. Sanchez-Carrera, V. Coropceanu, D.A. da Silva Filho, R. Friedlein, W. Osikowicz, R. Murdey, C. Suess, W.R. Salaneck, and J.L. Bredas, "Vibronic Coupling in the Ground and Excited States of Oligoacene Cations", Journal of Physical Chemistry, p. 18904, vol. 110, (2006). Published

V. Coropceanu, S.I. Boldyrev, C. Risko, and J.L. Bredas, "The Impact of Symmetric Modes on Intramolecular Electron Transfer: A Semiclassical Approach", Chemical Physics, p. 107, vol. 326, (2006). Published

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"Singlet-Triplet Splitting of Geminate Electron-Hole Pairs in Conjugated Polymers", Physical Review Letters, p. 0066803/1, vol. 93, (2004). Published

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Books or Other One-time Publications

Web/Internet Site

Other Specific Products

Contributions

Contributions within Discipline:

Our work provides a unique approach to the theoretical understanding of the electronic and optical properties of organic conjugated materials that are incorporated in new generations of electronic and opto-electronic devices. Two major characteristics of our approach are: (i) to rely on a strong feedback loop between theory and experiment; and, (ii) to use methods that take account of the full chemical structure of materials.

The impact of our program in the field can be assessed by the fact that Dr. Bredas served as Vice-Chair in 2006 and will serve as Chair in 2008 of the Gordon Research Conference on 'Electronic Processes in Organic Materials'. He ranks #36 on the list of most cited chemists for the period 1994-2004.

Contributions to Other Disciplines:

By providing an in-depth understanding of the electronic structure and optical properties of organic conjugated materials, our work impacts on the development and fabrication aspects of these materials into new generations of electronic and opto-electronic devices, such as plastic transistors and flexible displays.

Contributions to Human Resource Development:

Four female graduate students, including one African American, and one latino graduate student as well as one female postdoc and one female visiting scientist are currently members of our research group. Our group also provides for a very multicultural experience as thirteen nationalities are represented.

Of note is the requirement for each of our graduate students to spend two or three months, usually during their third year, in our sister laboratory at the University of Mons-Hainaut in Belgium. This provides them with a unique opportunity to broaden their graduate experience in Europe.

A major aspect of our program is to work on the development of a Materials Chemistry curriculum at the Georgia Institute of Technology. We are already contributing to such a project by teaching what has become a two-semester graduate course on 'Chemistry of Electronic and Optical Materials'. Also, an entirely new course on 'Applications of Quantum Chemistry to Electronic and Optical Organic Materials' has been developed, and taught for the first time during the 2005-2006 academic year.

One of our female graduate students has received a Georgia Tech Student and Teacher Enhancement Partnership (STEP) Fellowship for academic year 2004-2005 to help in the science education in local high schools. Part of her Fellowship was covered by our group.

We have also engaged in the GIFT program at the Georgia Institute of Technology. One local high-school teacher, Mrs. Anne Granville, has spent a significant amount of time doing research in my group during the 2004 summer, (with her stipend covered by our group). One of Mrs. Granville's students at Norcross High School, Justin Edward, has spent the following summer working half-time in our laboratory and being exposed to research; he has now applied for college at Georgia Tech.

Contributions to Resources for Research and Education:

There is significant industrial interest in our theoretical work on pi-conjugated materials by companies involved in device development and fabrication. Interactions with these companies help to broaden the perspective of the researchers in our group, so that they become more conscious of the potential impact of the basic research. We believe that the research program we conduct thus provides a sound and broad scientific training of students and will ultimately have a tangible impact on society.

Contributions Beyond Science and Engineering:

Categories for which nothing is reported:

Any Book

Any Web/Internet Site

Any Product

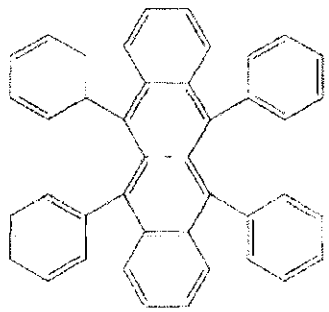
Contributions: To Any Beyond Science and Engineering

Major Research Findings

Understanding of the variations in the mechanisms of singlet and triplet exciton formation as a function of chain length in electroluminescent π-conjugated materials. The quantum efficiency for electroluminescence [photoluminescence], η_{EL} [η_{PL}], is defined as the ratio between the number of photons coming out of the device and the number of electrons injected [photons absorbed]. In π-conjugated oligomers and polymers, the ratio η_{EL}/η_{PL} is controlled by the fraction of singlet excitons generated in the diode. For a long time, this ratio was thought to follow simple spin multiplicity rules according to which η_{EL}/η_{PL} should not exceed 25% (since the recombination of an electron-hole pair – both spin ½ – leads to a total of four microstates with three triplet states and one singlet state). However, although the issue remains somewhat controversial, there has been compelling experimental and theoretical evidence that, *in conjugated polymers*, larger ratios between EL and PL quantum yields can be achieved. This stresses the possibility of producing highly efficient polymer LEDs and raises fundamental questions about the mechanisms determining exciton formation.

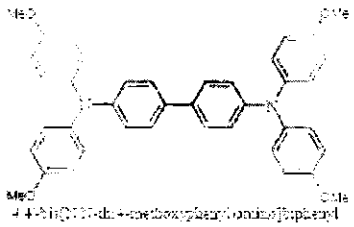
By evaluating the kinetics of the charge-recombination process from a polaron pair (forming a singlet or triplet charge-transfer, CT, state) into the lowest singlet S_1 or triplet T_1 exciton state, we were able to explore the *chain-length dependence* of the singlet and triplet formation cross-sections in conjugated materials. Short and long oligophenylenevinylenes were taken as model compounds. The main conclusions we reached can be summarized as follows: (i) Deviations from simple spin statistics occur when triplet charge-transfer excited states (polaron pairs) are amenable to intersystem crossing or dissociation; importantly, in a related joint experimental/theoretical work, we showed that the exchange energy within polaron pairs in conjugated polymers is small enough to make such an intersystem crossing process possible at room temperature. (ii) The electronic couplings between the CT states and the neutral exciton states are predicted to be largest for S_1 and T_1. However, because of the large exchange energy (S_1-T_1 energy difference), the probability for direct recombination into T_1 is, in all cases, very small (Marcus inverted regime). (iii) *In small molecules*, the CT-S_1 energy difference is large. Both singlet and triplet exciton formations proceed via higher-lying S_n/T_n states, which display similar electronic couplings and are therefore characterized by similar formation rates. These rates are fast and, as a result, spin statistics is expected to be obeyed. (iv) *In long conjugated chains*, the energy difference between the CT and S_1 excited states becomes on the order of the reorganization energy, *i.e.*, a few tenths of an eV; in a Marcus-type picture, this leads to the smallest barriers to recombination. As a result, the $^1CT \rightarrow S_1$ pathway tends to be even faster than in small molecules. On the contrary, the $^3CT \rightarrow T_n$ channels become much slower, leaving room for intersystem crossing (or dissociation) of the ^3CT states. This underlines the possibility of a significant *bias towards singlet exciton formation* and, therefore, of an η_{EL}/η_{PL} ratio over 25%.

Elucidation of the origin of high hole-carrier mobilities in rubrene single crystals. The high quality of rubrene crystals has recently allowed detailed measurements of the transport characteristics, including the observation of the Hall effect. Charge transport in rubrene single crystals, while trap-limited at low temperature, appears to occur via delocalized states over the 150 - 300 K temperature range with an (anisotropic) hole mobility of up to 20 cm^2/Vs at room temperature. Due to the bulky phenyl substituents attached to the side of the tetracene backbone (see sketch below), weak intermolecular interactions were expected in the material. The observation of large carrier mobilities thus came as a surprise. Therefore, in order to elucidate the origin of these mobilities and of their marked anisotropy along the crystallographic axes, we performed quantum-chemical calculations of the electronic structure of rubrene, both at the band-structure level and at the level of interacting dimers. In the latter case, we evaluated the evolution of the intermolecular electronic coupling as a function of the displacement of one oligomer

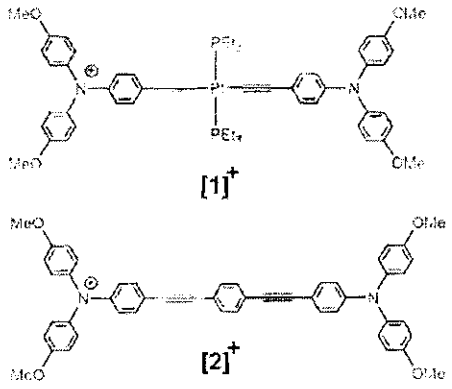


over the other. We found that the HOMO and LUMO couplings display a typical oscillating evolution upon displacement; the most remarkable result is that, when considering the large displacement (6.13 Å) observed along the stacking axis in the rubrene crystal, both HOMO and LUMO couplings are near peak values in their oscillations. This result clarifies why, even for such a large displacement, the electronic couplings are still a significant fraction of the values found for the cofacial case. This leads to a hole bandwidth of *ca.* 0.4 eV, which is confirmed by the results of the calculation of the three-dimensional electronic band structure of the rubrene crystal with the Plane-Wave Density Functional Theory (DFT) method.

Thorough characterization of organic mixed-valence (MV) systems. While studying inter-molecular electron-transfer processes in organic transport materials, it occurred to us that in a number of instances, these materials actually display interesting *intra*-molecular electron-transfer processes. This is the case, for instance, in bis-triarylamines (used for hole transport) or bis-dioxaborines (considered for electron transport), since each molecule presents two redox sites. In the case of the bis-triarylamines (see sketch below), these are the two nitrogen atoms: As a function of the nature/length of the bridge between the nitrogens, the positive charge appearing in the radical-cation state can either be localized on one of the nitrogens (in the classification of Robin and Day, this corresponds to a class-I system if localization is complete or a class-II system if there occurs hopping between the two sites) or be completely delocalized (class-III system). The extent of localization/delocalization depends intimately on the relative strengths of electronic coupling (which favors delocalization) vs. vibronic coupling (which favors localization). Over the past two years, we made significant progress in the characterization of such organic mixed-valence systems:



(i) We showed that the electronic coupling in strongly coupled organic mixed-valence systems can be effectively probed by means of gas-phase ultraviolet photoelectron spectroscopy (UPS). Taking six bis-triarylamines as examples, the UPS electronic couplings were found to be somewhat smaller than those derived from optical spectroscopy. Interestingly, we were able to attribute this difference to the role of vibronic coupling to symmetrical modes.



(ii) Organometallic 'rigid-rod' polymers with π-conjugated metal-organic units, notably Pt-alkynyl polymers, have received attention due to their potential use as advanced electronic materials. It is well recognized that the performance of electronic devices is influenced to a large extent by the efficiency of intrachain electron and hole migration or delocalization. However, the question concerning the degree to which a metal atom such as Pt disrupts (or enhances) the π-conjugation between organic units and hence alters the electronic structure remained to be fully addressed. Our joint experimental/theoretical work provided a *quantitative* assessment of the effect Pt has on electronic delocalization by comparing a system in which two triarylamine redox centers are bridged by Pt, $[\mathbf{1}]^+$, to an all-organic structural analog reported earlier, $[\mathbf{2}]^+$ (interestingly, while inorganic MV systems with both inorganic and organic bridges have been much studied and pure organic MV systems are gaining increasing attention, to the best of our knowledge, $[\mathbf{1}]^+$ is the first reported MV system where two organic redox centers are coupled through a metal atom). We were able to show that the electronic coupling through an alkyne-Pt-alkyne bridge is only very slightly smaller than through an alkyne-benzene-alkyne bridge. This leads to the conclusion that electronic delocalization in Pt-alkynyl π-conjugated polymers is not substantially decreased when compared to poly(phenylene-ethynylenes) and,

hence, the phosphorescent properties imparted to the system by Pt do not seem to be outweighed significantly by a deleterious reduction in conjugation along the polymer chain.
(iii) We carried out an investigation of the dependence of the electronic coupling between the two arylamino redox sites as a function of the length of the bridge; we considered bridges corresponding to oligophenylenes containing from n=2 (that is, stilbene) to n=5 phenylene rings. While both theory and experiment show that the radical-cation of the n=2 compound is a delocalized class-III or class II/III-borderline mixed-valence species (indicating that the electronic coupling is stronger than, or at least of the same order as the vibronic coupling), the n=3 radical-cation is a class-II mixed-valence species (indicating that the vibronic coupling has already become dominant for such a bridge length). In the radical-cations of the longer n=4,5 species, the nitrogens are no longer electronically coupled to any significant extent. The corresponding dications show a complementary trend in the coupling between redox centers: the shortest species is diamagnetic, while the dication with the longest bridge behaves as two essentially non-interacting radical centers.
(iv) We examined the interplay between bridge energy and geometric factors by considering three organic arylamino-based mixed-valence systems that possess nearly identical inter-redox site distances and differ by the nature of the bridging units: benzene, naphthalene, and anthracene. The results of gas-phase UPS, Vis/NIR spectroscopy, and electronic-structure calculations concur to indicate that the strength of electronic interaction decreases in the following order of bridging units: benzene > naphthalene > anthracene. This finding contradicts the usual expectation that anthracene is superior to benzene as a driving force for electronic communication. We were able to explain these results in terms of a super-exchange mechanism and its strong dependence on steric interactions, the larger bridges leading to higher rotation angles between the conjugated segments.

Characterization of discotic liquid crystals. Discotic liquid crystals have emerged as attractive materials for organic-based (opto)-electronics as they allow for efficient charge and energy transport along self-organized molecular columns. In a joint experimental/theoretical work, we investigated the electronic structure and supramolecular organization of the discotic molecule, hexakis(hexylthio)diquinoxalino[2,3-a:2',3'-c]phenazine (HATNA-SC_6) deposited on graphite, via angle-resolved UPS and quantum-chemical calculations. The UPS data revealed significant changes in the electronic properties when going from disordered to columnar phases, the main feature being a decrease in ionization potential by 1.8 eV following the appearance of new electronic states at low binding energy. This evolution was rationalized by the calculations, which indicated the formation of a quasi-band structure with Bloch-like orbitals delocalized over several molecules in the column. Interestingly, the data point to an energy dispersion of the upper π-bands in the columns by some 1.1 eV, therefore highlighting the strongly delocalized nature of the π-electrons along these discotic stacks.
We also described at the quantum-chemical level the main parameters that control charge transport at the molecular scale in a series of discotic liquid crystalline stacks made of triphenylene, hexaazatriphenylene, hexaazatrinaphthylene, and hexabenzocoronene molecules. We illustrated how a fine interplay between the chemical structure of the molecules and their relative positions within the stacks determines the charge transport properties; the molecular features required to promote high charge mobilities in discotic materials were established on the basis of the calculated structure-property relationships. The calculations predicted an increase by one order of magnitude of the charge mobility when going from triphenylene to hexaazatrinaphthylene; importantly, these results were later confirmed by mobility measurements, which gives much confidence in our theoretical approach.

Interchain vs. intrachain energy transfer in conjugated polymers. The limitations of the traditional point-dipole Förster model to describe energy transfer in conjugated polymers, were illustrated in the case of a simple system consisting of two interacting chains, a pristine ladder-type poly(*para*-phenylene), LPPP, chain and an LPPP-chain bearing a ketonic defect. The latter chain displays both localized electronic excitations close to the ketonic sites as well as excited states that are delocalized over the whole

conjugated chain. The traditional Förster model was found to fail completely in describing energy transfer between a delocalized and a localized state.
We thus kept refining our theoretical description of exciton migration in conjugated polymers on the basis of an improved Förster model. In the improved model, the rates are expressed according to Fermi's Golden Rule, by considering: (i) electronic couplings that take account of the detailed shape of the excited-state wavefunctions through the use of a multicentric monopole expansion; and (ii) spectral overlap factors computed from the simulated acceptor absorption and donor emission spectra with explicit coupling to vibrations (considered within a displaced harmonic oscillator model); inhomogeneity is taken into account by assuming a distribution of chromophores with different conjugation lengths. We have explored the dynamics of *interchain* vs. *intrachain* excitation energy transfer taking place in a polyindenofluorene end-capped with perylene derivatives by means of ultrafast spectroscopy combined with correlated quantum-chemical calculations. The experimental data indicate faster exciton migration in films with respect to solution as a result of the emergence of efficient channels involving hopping between chains in close contact. These findings are supported by our theoretical simulations which predict faster *intermolecular* energy transfer as a result of larger electronic matrix elements and suggest a two-step mechanism for *intrachain* energy transfer with exciton hopping along the polymer backbone as the limiting step. Injecting the calculated hopping rates into a set of master equations allowed the modeling of the dynamics of exciton transport along the polyindenofluorene chains and yielded ensemble-averaged energy transfer rates in very good agreement with experiment.

A first attempt at describing fully quantum-chemically the photoinduced charge-generation and recombination dynamics in donor/acceptor complexes. We developed a theoretical methodology that allowed us to estimate the molecular parameters that determine the rates of two processes, exciton dissociation and charge recombination, of importance in organic solar cells. The general concepts behind our approach were illustrated by considering a donor-acceptor complex made of a phthalocyanine (electron-donor) molecule and a perylene (acceptor) molecule. The results revealed the dependence of the relative rates of the two processes on the dimensionality of the molecules, their relative positions, the symmetry of the relevant electronic levels, and the polarity of the medium. It was found, for instance, that highly symmetric configurations of the complex strongly limit charge recombination.
At the present stage, however, our methodology is limited since it is able to consider the electronic coupling between just two states (the relaxed photo-induced excited state and the lowest, strongly Coulomb-bound charge-transfer state) and it assumes negligible coupling between these states. Therefore, we will briefly describe below a new theoretical approach that aims at removing these limitations.